Synergistic effects of clay and GNPs on electrical and mechanical properties of PU/GNP/OMMT ternary composite

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Ternary nanocomposites based on nanograpite platelets, OMMT and polyurethane were prepared using in-situ polymerization with the aim of achieving low percolation threshold and improving the electrical and mechanical properties. The nanocomposites were evaluated for their electrical and mechanical properties and the results were compared with the corresponding binary systems, i.e., PU having GNP as the only filler. It was observed that the addition of OMMT at a concentration of around 2 wt%, significantly enhances the electrical and mechanical properties of the nanocomposites with the percolation threshold at much lower concentration of the GNPs. The excellent electrochemical properties arise due to formation of new 3D network (clay-graphite-clay or graphite-clay-graphite) and the synergistic effect between the three components.

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1. Introduction

In the recent year a lot of research has been done to study the synergistic effects of two nanofillers in one system. The two key factors associated with nanofillers are their proper dispersion in the matrix and strong interfacial interaction with the matrix. According to previous studies, PU/nanofiller binary nanocomposites drew attention because of their interesting and fine-tuned properties. [1]. However, the PU based ternary nanocomposites are less studied. Ternary nanocomposites are anticipated to show more versatile properties and higher potential in applications.

Carbon nanotubes, carbon black, graphite nano particles are considered excellent fillers because of their conducting properties [2]. However, being inert, these conductive fillers are not properly dispersed in the matrix and get agglomerate at higher loading level (beyond percolation threshold). Further, as the concentration of conductive filler increases above percolation threshold, the mechanical properties of prepared nanocomposites also start to deteriorate because the agglomerated part of conductive filler acts as the stress concentration area leading to poor mechanical properties like decrease in strength and modulus of the nanocomposites [3]. The poor interface interaction with matrix along with poor dispersion leads to poor mechanical as well as electrical properties. The preparation of multifunctional, high performance nanocomposite which having good electrical (low percolation threshold) as well as mechanical properties can overcome these limitations. Various methods are available in literature to lower down the percolation threshold of CNTs in polymers like use of additives, the optimization of processing conditions and managing the size distribution [3] and the use of multiphase polymer blends [4]. Recently Seung Bin [5] attempted to lower down the percolation threshold of CNTs by using an immiscible polymer blending approach and mechanofusion technique. Synergistic effects of CNTs and layered double hydroxide (LDH) nanoplatlets in nylon matrix with improved mechanical properties were studied in [6]. A similar approach of using a second filler/nanofiller working in a synergy with CNT has been proposed by [7], and is defined as mixed (nano) filler system.

Recently, utmost attention is being directed to the use of CNTs with clay as binary filler. Polymer nanocomposites using clay/silica nanoparticles [8], clay/carbon black nanoparticles [9], and CNTs/titanium [10], have been prepared. Adding clay into the nanotube/EVA composite has shown to enhance the formation of graphitic carbon. [11] Poly(methyl methacrylate)/silica/titania ternary nanocomposites with greatly improved thermal and ultraviolet-shielding properties were prepared by Haitao Wang et al. [12]. A ternary cobalt ferrite/graphene/ polyaniline nanocomposite is synthesized for high-performance supercapacitors [13]

In this paper, we report the preparation and characterization of PU/OMMT/GNPs ternary nanocomposites by using in situ polymerization technique.

The synergistic effects of both the fillers were studied on electrical (percolation threshold) and mechanical properties of prepared nanocomposites. An effort has been made to retain the mechanical properties by lowering down the percolation threshold. The results were compared with the corresponding binary systems, i.e., PU having GNP as the only filler and significant improvement of the electrical and mechanical properties has been observed in ternary nanocomposites. A plausible explanation has been given to explain the observed improvements.

2. Experimental section

2.1 Materials

Cloisite-30B was supplied by Connell Bros. Company (India) Pvt. Ltd. The graphite used for preparing GNPs was GIC, acidified with concentrated H_2SO_4 and HNO_3. The monomers Toluene, 2,4-Diisocyanate (TDI) with molecular weight 174.16 and Polypropylene glycol (PPG) with molecular weight 2000 were supplied by MP Biomedicals Fine Chemicals Division, India. The monomers were of analytical grade purity and were used as received. The chain extender 1,4-Butanediol (BDO) was supplied by same company. 95% (v/v) alcohol and distilled water were used as solvents for preparation of GNPs.

2.2 Preparation of Expanded Graphite and Graphite Nano Sheets

Expanded graphite was prepared by adopting the procedure reported by [14,15]. The GIC (powder form) was given a thermal shock at 1050 ^{O}C for 15 seconds in a muffle furnace to obtain expanded graphite particles along c direction or thickness direction about several hundred times that of original c direction dimension [16]. The gallery space of expanded graphite expands due to evaporation of intercalants trapped between the layers. The expanded graphite so obtained was mixed and saturated with 400 ml alcohol and distilled water in a ratio of 70:30 for 8 h. This mixture was subjected to sonication using a horn type sonicator for various time intervals (5, 8, 10 and 12 h). After sonication, expanded graphite particles were effectively fragmented in to foliated graphite. The graphite nano sheets dispersion was then dried at 80 ^{o}C to remove the residual solvents. In this way, the graphite nano sheets were obtained to be used as nanofiller in proposed nanocomposites.

2.3 Preparation of Polyurethane Graphite Composites by In-Situ Polymerization

The PU/GNPs/OMMT composites were prepared by using TDI:PPG:BDO in the mole ratio of 3:1:2. PPG and prepared GNPs were mixed with Cloisite-30B and stirred for 12 h at 50^{o} C to obtain PPG-GNPs-OMMT suspension. This suspension was subjected to sonication for one hour to avoid the agglomeration of graphite nano particles. The viscosity of PPG maintains a uniform distribution of particles in the solution. TDI was poured in to this suspension with continuous stirring. During the mixing of TDI, the temperature was maintained at 70o C as it was an exothermic reaction. After mixing TDI, the resultant solution was heated at 85^{o} C for 4 h with stirring. Subsequently, after cooling the reaction mixture to 40^{o} C, BDO was added with vigorous stirring for 1 min. immediately after this, a small portion of solution was mixed with DMF for spin coating and TEM characterization. The resultant composite solution was poured into a defined shape mold for final curing. The composite material in the mold was heated at 160^{o} C for 16 h to dry it completely. To do the comparative studies of properties on equal dimensions, the dimensions of prepared samples are maintained by use of equal sized molds. Similarly, all spin coated films are made using the same dimensions of glass/silicon substrates. The dispersion state of prepared nanocomposites samples was studied by Transmission Electron Microscope (TEM). The samples were prepared by dispersing the film on glass/silicon substrates by spin coater. The mechanical properties of prepared nanocomposites samples were studied by universal testing machine.

2.4 Characterization

To have an idea about the dispersion of both the fillers in the matrix X ray diffraction (XRD) patterns of prepared nanocomposites were recorded on PANalytical's XPERT-PRO Diffractometer system with Cu K-Alpha1 [Å]: 1.54060 and 2θ (3^{o}- 40^{o}). The dispersion of both the fillers, was further confirmed by TEM images. The surface morphology of the nanocomposites was studied by SEM. The electrical properties of prepared samples were studied by four point method and effect of addition of clay on percolation threshold was observed. The mechanical properties of these prepared samples using binary fillers were studied by universal testing machine, and were compared to nanocomposites of PU/GNPs and PU/OMMT.

3. Results and Discussion

3.1 XRD Analysis

The results of XRD are shown in Figure 1, in the form of diffraction peaks of GNP, Cloisite 30B, and ternary nanocomposites containing GNP and Cloisite-30B as binary fillers. The pure GNP and pure Cloisite-30B has displayed the sharp intended peaks at 26.3^{o} and 4.81^{o} indicating D- spacing of 3.38 Å and 18.32 Å respectively. As disappearance of major diffraction peak of filler indicates the exfoliation morphology and shifting of diffraction peak towards lower angle with reduced

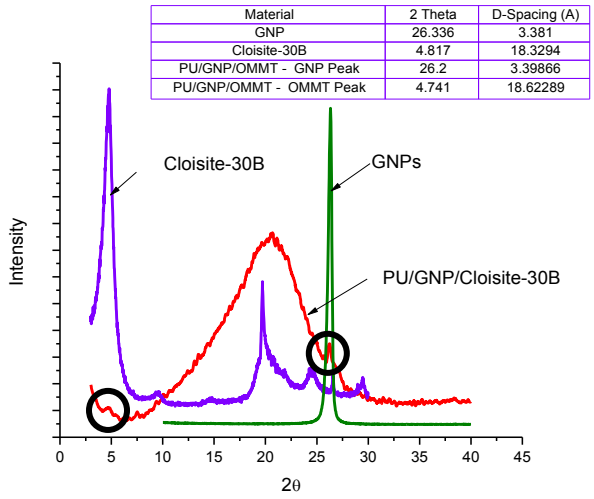

Fig.1. X-ray Diffraction of GNPs, Cloisite 30B, and Prepared Samples of Ternary Composites

intensity indicates the intercalated morphology of nanocomposites. Based on these facts our prepared ternary nanocomposites revealed an intercalated type of morphology as the major diffraction peaks of both the fillers have shifted towards lower angle with much reduced intensity. A broaden peak in nanocomposite sample near 20^{o} indicates the peak of PU, means the crystallinity of matrix has not been effected by dispersion of these two fillers. The dispersion was further confirmed by TEM images of nanocomposites.

3.2 SEM and TEM Analysis

The surface morphology of prepared PU/GNPs/OMMT ternary nanocomposites was absorbed by SEM at different magnifications as shown in Figure 2. At low magnification the GNP and clay particles are well dispersed in the matrix. It can be seen that clay particles are anchored on the surface of GNPs, making a continuous conductive network in the matrix, which helped to lower down the percolation of nanocomposite (Fig. 2 (a) and Fig. 2 (b). At high magnifications, the roughness of surface can also be seen due to presence of GNPs of different sizes. The bundles of GNPs can also be seen at high magnification and are well connected to each other which again helped to lower down the percolation threshold of nanocomposite. At the same time pulled out graphene bundle can also be seen at some places showing not a good adhesion between GNPs and matrix at those points (Fig. 2 (c) and Fig. 2 (d)). The intercalated GNP particles are shown in Figure 3(a) TEM image. The intercalated clay is shown in Fig. 3 (b). The stack of graphene layer can be easily seen In the Fig. 3(c). The d-spacing can also be calculated from the profile of fringes is shown in the inset of Figure 3(c). Individual layers of graphite are clearly visible as regions of alternating narrow, dark and light bands within the particles (fringes) as shown in Figure 3(d) along with the live FFT the inset of Figure 3 (d).

3.3 Electrical Conductivity and Percolation Threshold Measurement

The prepared polymer composites are conducting in nature as they contain conducting filler and insulating matrix. These composites are capable of dissipating electrostatic charges and shielding devices from electromagnetic radiation. Due to good adhesive properties of polyurethane, these composites can be used as interconnection wires in integrated devices. In general there is a rapid increase in the electrical conductivity of prepared composite when a conductive network is formed

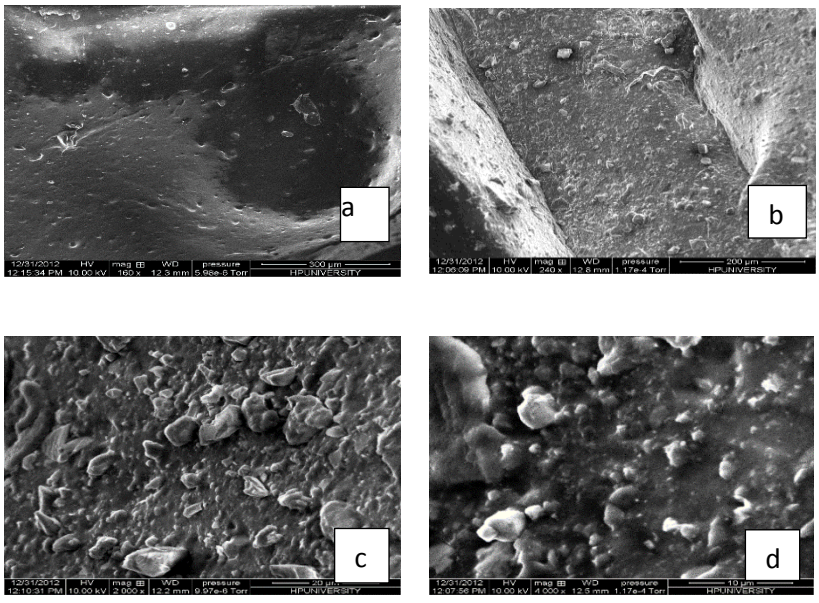

Fig. 2. SEM images of prepared PU/GNPs/Cloisite-30B composites.

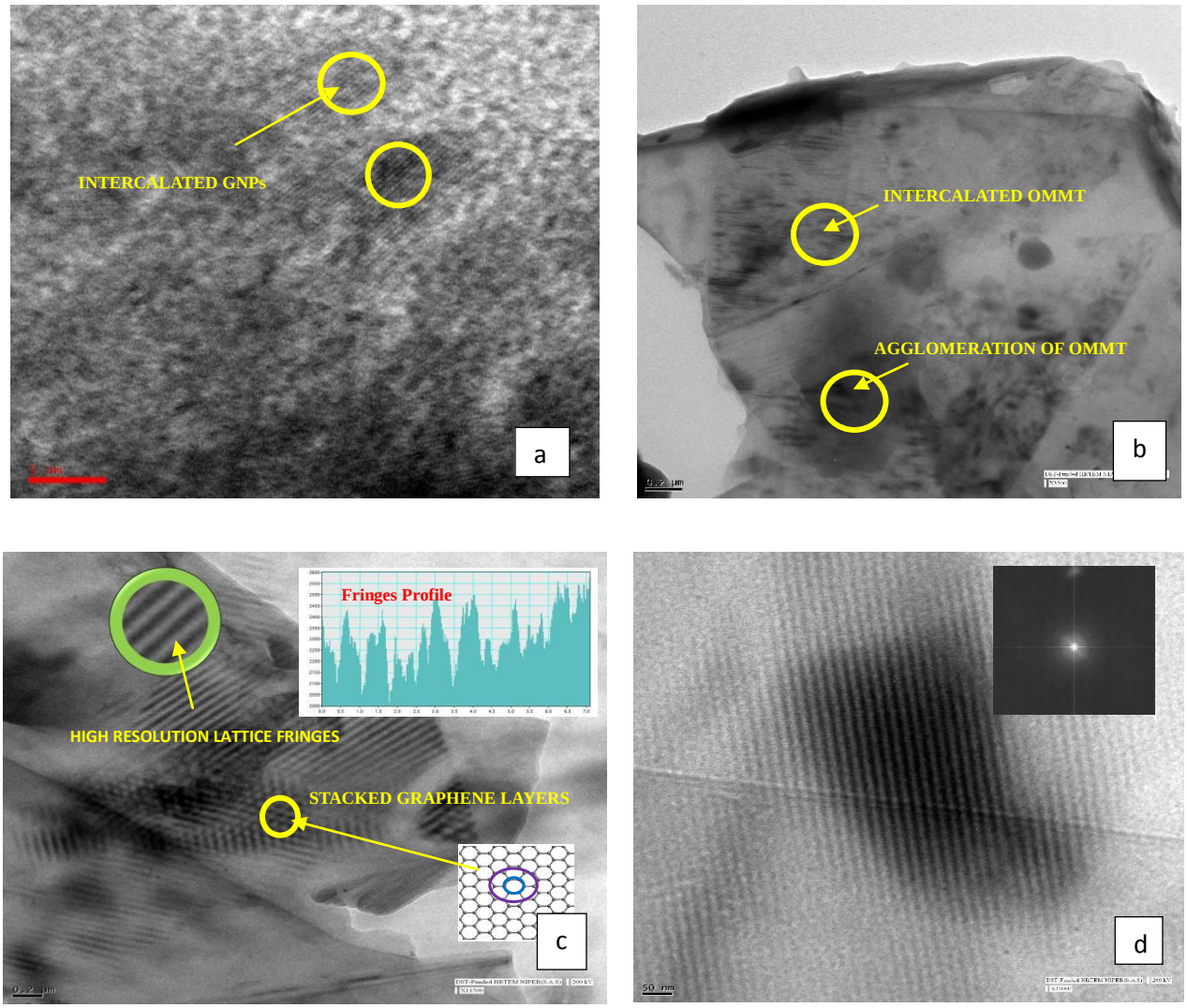

Fig. 3. TEM images of prepared PU/GNPs/Cloisite-30B composites

by the conductive fillers. It causes a transition in composite material from insulator to conductor [17]. The fraction of filler material at which there is as establishment of multiple, continuous electron path or continuous electrical network, is called percolation threshold. In order to maintain the electrical conductivity of composite containing insulating matrix, the concentration of conducting filler must be equal or greater than the percolation threshold. However this percolation threshold is lower down in case of ternary nanocomposites as shown in Figure 4. In this paper an effort has been made to lower down the percolation threshold by addition of OMMT along with GNPs as binary fillers. It was found out that with the addition of 2wt% of clay (calculated from the vol% of clay using its density), the percolation threshold is reduced to 0.6 vol% from 2.2 vol%. With this reduction in percolation the electrical conductivity is also increased at different loadings of GNP with constant fraction of OMMT. This improvement in electrical conductivity as well reduction in percolation threshold may be due to presence of clay increases the melt viscosity of the matrix polymer, and thus shear force during mixing, which helps to better dispersion of the GNP[1]. The electrical behavior of the composite is explained on the basis of percolation theory [18]. According to this theory, near the percolation threshold, the electrical conductivity of the composite follows the following power law relationship.

$$\sigma = \sigma_0 (V_f - V_c)^s \quad (1)$$

Where σ the electrical conductivity of the composite, σ_0 is the electrical conductivity of the filler, V_f is the filler volume fraction, V_c is the percolation threshold and s is a conductivity exponent. According to the tunneling mechanism, conduction can take place via tunneling between thin polymer layers surrounding the filler particles. Percolation threshold of GNP reinforced polymer is much lower than other carbon fillers like carbon fibers and carbon black, due to extremely large

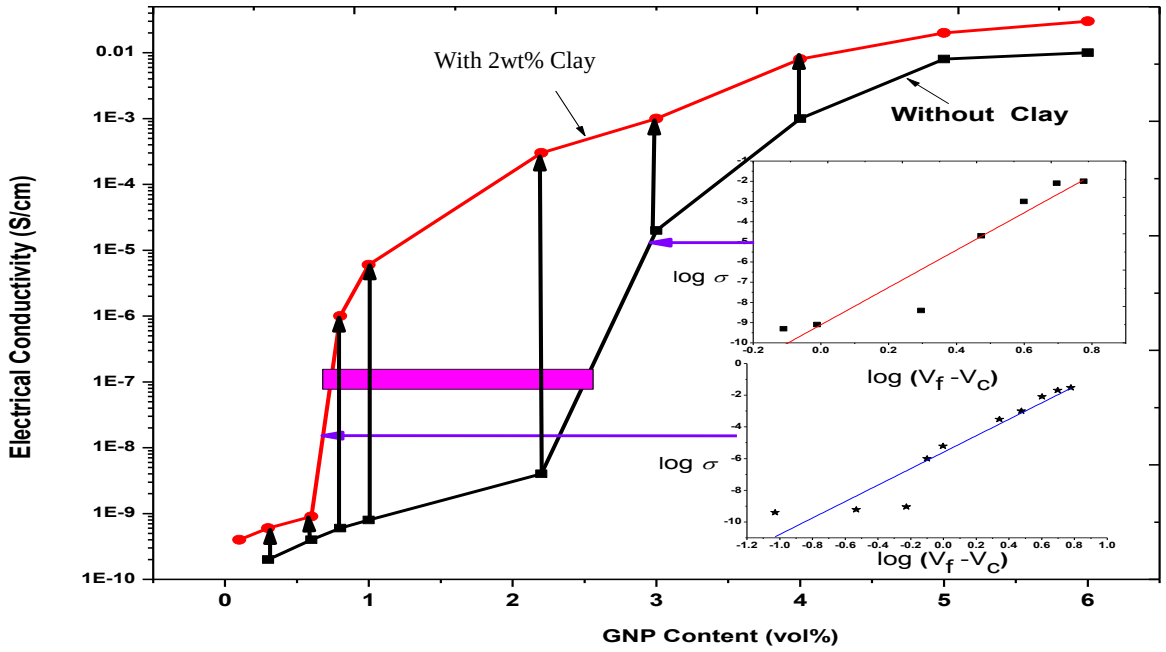

Fig. 4. Electrical conductivity of PU/GNPs and PU/GNPs/Cloisite-30B composites as a function of GNP content

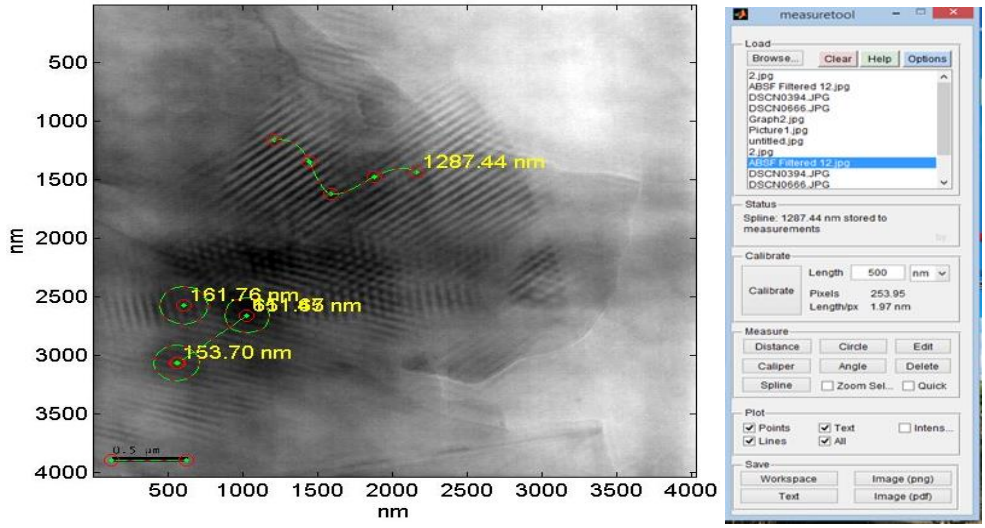

Fig. 5. Geometrical orientations measurement for IPD using Matlab

surface area and high aspect ratio of GNPs. As per the power law in Equation 1, the plot of log σ versus log (Vf - Vc) is drawn and shown in the inset of Fig. 4. The best linear fit is found for Vc = 0.022 without clay and Vc = 0.006 with clay. Here the power law for the conductivity values is well obeyed above the percolation threshold. The improvement in electrical properties along with the reduction in percolation threshold shown in Figure 4 is maximum with 2wt% fraction of clay as shown in Fig. 6. Further increase in clay loading reduces the electrical conductivity gradually. May be, above this loading of clay, which is non-conducting in nature, the insulating clay platelets plays an important role , formation of hybrid network path of GNP and insulating clay silicates.

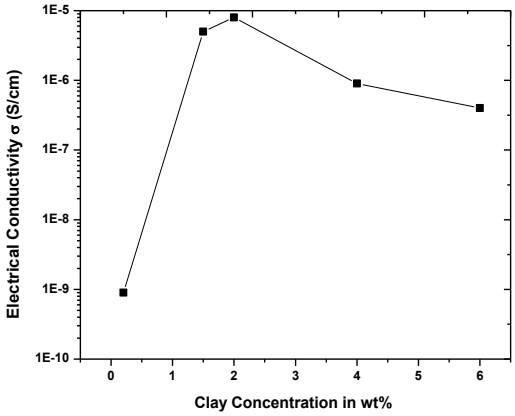

Fig. 6. Effect of clay concentration on electrical conductivity of ternary nanocomposite

The percolation threshold is further validated analytically by measuring the inter particle distance (IPD) using Matlab. The volume fraction, P, of GNP is given by [19]:

$$P_c = \frac{27\pi D^2 t}{4(D+IPD)^3} \quad (2)$$

Where D and t are the diameter and thickness of GNP with clay dispersed individually in the matrix. To create an electrical network in nanocomposite, filler particles must be overlapped in the thin polymer layers as shown in the TEM images of composite in Figure 3. For overlapped particles D>>IPD, is measured by matlab tool. Equation 2 then reduces to:

$$P_c = \frac{27\pi t}{4D} = \frac{21.195}{\alpha} \quad (3)$$

Where α is the aspect ratio. The value α can be determined using Image J [20].

3.4 Mechanical properties

The mechanical properties of ternary nanocomosites were studied, and compared to binary nanocomposites

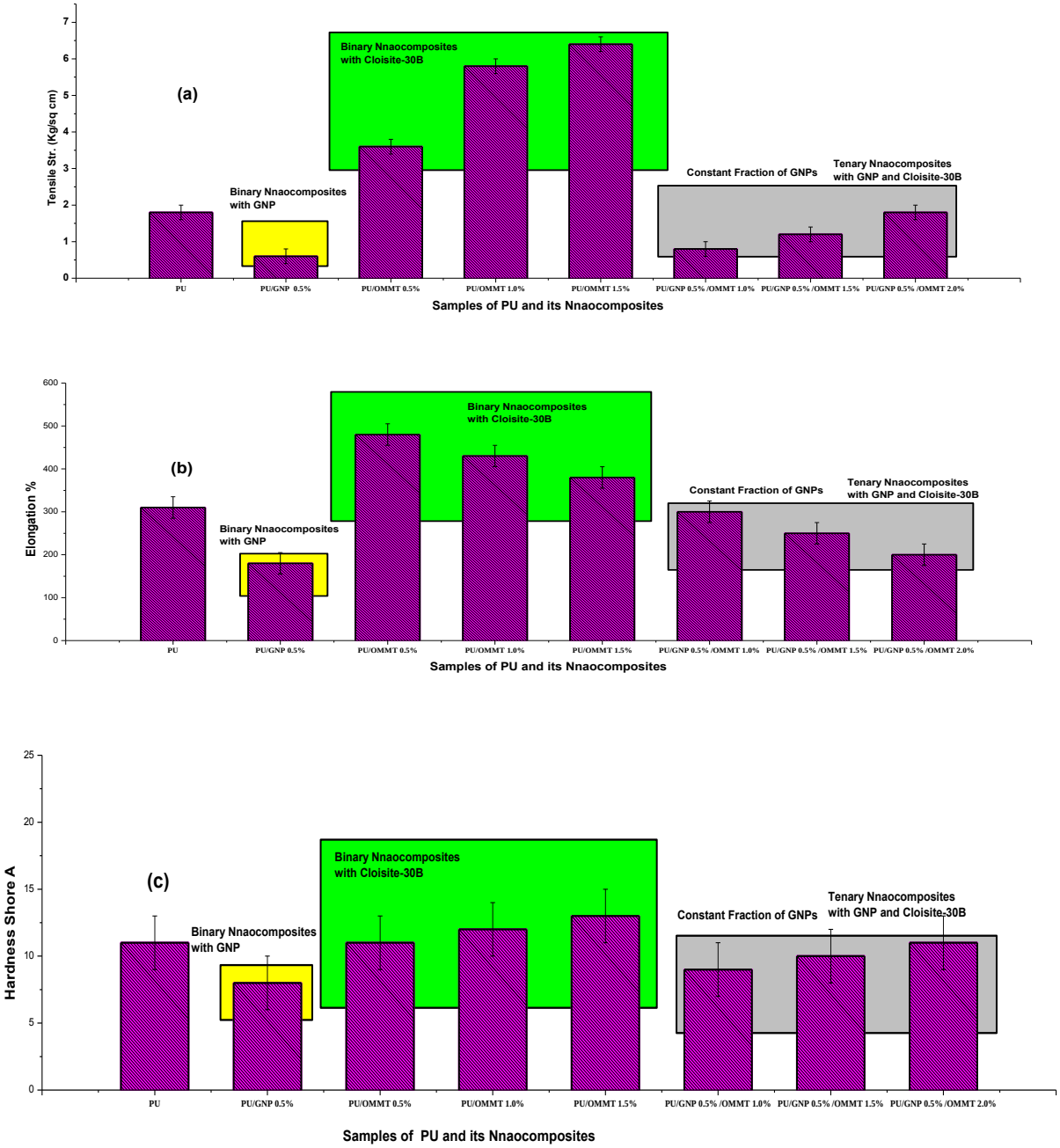

Fig. 7. Mechanical Properties of PU/OMMT and PU/GNPs/OMMT Nanocomposites (a) Tensile Strength (b) Elongation % (c) Hardness Shore A

PU/GNPs, PU/Cloisite-30B, and pure PU respectively. It was observed at fraction of GNPs (0.5 wt%) the tensile strength get decreased as compare to pure PU. In order to get good tensile strength at this fraction of GNP along with the improved electrical properties, the OMMT was added with different loading levels by keeping this GNP fraction constant at 0.5 wt%. It was observed that upon addition of clay the tensile strength was increased upon increasing the loading level of OMMT. But this increase in tensile strength was very less as compare to PU/OMMT binary nanocomposite as shown in Fig. 6(a). In ternary nanocomposite at 2.0 wt% of clay, the tensile strength was found almost equal to pure PU. The addition of clay at different loading in ternary nanocomposite may leads to uniform stress distribution from matrix to filler due to their uniform dispersion. It can be said that there must be formation of interconnected hybrid network of GNP-clay-GNP or clay-GNP-clay which helped to reduce the agglomeration of GNPs and improve the uniform distribution of stress. An opposite trend was observed for elongation % as compare to tensile strength. The elongation % decreases with increase in loading level OMMT at constant fraction of GNPs as shown in Figure 6 (b), and was less than pure PU at all loading levels of clay. Shore hardness is a measure of the resistance of a material to the penetration of a needle under a define spring force. The letter A is used for flexible type. The hardness shore A is also increased with the increase in % loading levels as compare to pristine PU [21]. At 0.5 wt% loading level of OMMT, the harness shore A was maintained at a level closed to that of pure PU. At 1.0 and 1.5 wt % of OMMT, a slight increase in hardness has been observed. The hardness shore A also increases with increase in loading level OMMT at constant fraction of GNPs as shown in Figure 6 (c), and was equal to that of pure PU at 2.0 wt% loading level of clay as shown in Figure 6(c).

4. Conclusion

Ternary nanocomposites reinforced with OMMT and GNPs as binary fillers were prepared by in-situ technique to observe the effect of addition of OMMT on percolation threshold and mechanical properties as compare to composite containing GNPs alone. SEM indicated a satisfactory dispersion of OMMT and GNPs with the matrix revealing a good interfacial bonding between fillers and the matrix. The TEM and XRD revealed the formation of intercalated type of ternary nanocomposites. The percolation threshold was lowered to 0.6 vol% with addition of 2 wt% of OMMT. Wt % is calculated using $vol\%filler = wt\%filler/\left[wt\%filler + wt\%matrix(\frac{\rho_{filler}}{\rho_{matrix}})\right]$. This was much lower as compare to percolation threshold of nanocomposite containing only GNPs as filler (2.2 vol%) with this improvement in percolation threshold, the electrical conductivity was also increased. The optimized electrical properties were found at 2 wt% loading of clay, further increase in clay concentration lead to decay in electrical conductivity. Along with electrical properties, the effect of addition of OMMT was also studied for mechanical properties. It was observed that tensile strength and hardness shore A were increased as compare to PU/GNP nanocomposites but were lower than PU/OMMT nanocomposites. An opposite trend was found for elongation %. The elongation % decrease with the increase in loading levels of clay at constant fraction of GNPs (0.5wt %) in ternary nanocomposites. The aim of this work was to prepare a ternary nanocomposite with lower percolation threshold with good mechanical properties as compare to composite containing GNPs alone, which was satisfactory achieved. The possible application of such ternary nanocomposites packaging in integrated circuits, micro sensors, and MEMS, where both electrical and mechanical properties are required.

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